



Wireless Electrochemical ClO_2 Monitor for Decontamination Operations

Mourad Manoukian ¹

¹Giner, Inc. 89 Rumford Ave, Newton MA, 02466



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Problem Statement

The U.S. Environmental Protection Agency (EPA) has identified the need for a portable, accurate and field rugged chlorine dioxide (ClO_2) monitor for use in monitoring building decontamination operations.

Chlorine dioxide played a major role in 2001 when it was used to destroy deadly spores of the bacterium *Bacillus anthracis* in the United States Senate Office Building in Washington, DC. Decontamination of the Hart Senate Office Building was successfully achieved by circulating ClO_2 gas throughout the building, destroying the *Bacillus anthracis* spores. The EPA recommended decontamination method includes treatment with 500-750 ppm of ClO_2 for a minimum of 12 hours.

The primary method of ClO_2 determination in work-place atmospheres, that is approved by the Occupational Safety and Health Administration (OSHA), is ion chromatography.

There are a number of commercially available ClO_2 sensors based on colorimetric or electrochemical detection technique that sell for \$2500-\$3500. The main disadvantage of these systems is that they lack low level detection limit (<100 ppb) and they are relatively expensive. To the best of our knowledge, none of the electrochemical sensors commercially available use solid polymer electrolyte proton conductors integrated with screen printed electrodes. These devices use liquid acid electrolytes which are highly corrosive, reducing the operational life of the sensor.

Giner, Inc., proposes to develop a novel, continuous unattended and/or hand held electro-chemical ClO_2 monitor that is inexpensive (<\$100 to manufacture for quantities greater than 10,000 units) and is capable of monitoring ClO_2 levels in building decontamination operations, in real-time. The proposed instrument will be designed for wireless data transmission and could be used for building monitoring applications and to control concentration levels of ClO_2 gas generated for decontamination and fumigation applications.

Technology Description

The technical approach we have chosen to develop the proposed advanced, novel electrochemical ClO_2 sensor will be to extend, with modification, Giner, Inc.'s solid-polymer electrolyte-based sensor technology for the detection of ClO_2 . Complete sensor cells based on electrochemical reduction of ClO_2 will be fabricated and evaluated. The Giner, Inc. water-based solid-polymer electrolyte sensors fabricated with proton exchange membrane and electrode assemblies (MEAs) show excellent response time, magnitude, reproducibility and endurance.

Sensor cells will be developed comprising of solid-state proton-conducting electrolyte membrane pressed against screen-printed thick-film or sputtered thin-film platinum sensing, counter and reference electrodes. Using a potentiostatic circuit a constant potential will be applied between the sensing electrode, where ClO_2 is electrochemically reduced, and a stable reference electrode. Oxygen is evolved on the counter electrode.

This electrochemical reduction on the sensing electrode and oxidation on the counter electrode causes an ionic current to flow through the sensor which is proportional to the concentration of electro-reduced ClO_2 . This electro-reduction current is measured as current or voltage across a resistor from the sensor cell.

The technical innovation of the proposed advanced sensor cell will be the use of solid polymer electrolyte (no liquid electrolytes) and the unique integration of this solid polymer electrolyte with thick- or thin-film electrodes for a significantly improved detection limit (2 ppb). The sensor cell will be integrated with the low-noise potentiostatic electronic control and signal processing circuit, for optimum signal to noise ratio for the sensor response, and its performance will be demonstrated with a wireless data transmission system.

Expected Results

The Phase I program will establish the feasibility of an advanced electrochemical ClO_2 monitor for the selective and rapid detection of ClO_2 . The proposed advanced electrochemical monitor will have a detection range of 0 to 3000 ppm ClO_2 , with a detection limit of 2 ppb. In Phase I, the electrochemical ClO_2 sensor cell will be integrated with the potentiostatic electronic control and signal processing circuit and its operation demonstrated with wireless data transmission.

The Phase I feasibility studies will include detailed studies for specificity of the advanced sensor to ClO_2 in the presence of various common substances including many that might be expected to be present in the building environment (CO_2 , H_2O , CO , and NO_x). Comprehensive testing of other potential trace interferants and methods to filter them out or eliminate their effect by adjusting the operating parameters, such as sensing electrode composition and the applied potentiostatic voltage to the sensing electrode, will be conducted in Phase II in consultation with EPA.

In Phase II, comprehensive lifetime testing of the sensor will be conducted. Based on our previous experience with electrochemical sensors, we anticipate a useful sensor operating lifetime of at least 3 years. The end result of the Phase II developmental work will be a compact, light-weight and handheld instrument that will allow for continuous unattended or handheld independent operation of the monitor, complete with calibration routine and digital display of numeric results. The monitor will be battery operated with an AC converter and battery re-charger and will allow for wireless transmission of test data to a computer, in a central location, for remote documentation of test results. **To the best of our knowledge there is no commercially available and low-cost (<\$100 to manufacture in quantities greater than 10,000 units) hand-held electrochemical ClO_2 monitor capable of measuring 0 – 3000 ppm of ClO_2 in real-time with a detection limit of 2 ppb.**

In Phase III, the instrumentation will be tailored for specific uses to make the instrument commercially available in the dual use markets (e.g., food industry and water treatment).

Potential Environmental Benefits

In addition to its use as an antimicrobial agent in the gas phase, ClO_2 is also used to disinfect water. In applications in drinking water, chlorine dioxide is generated on an as needed basis by a controlled chemical reaction, such as the reaction of acid with sodium chlorite or the reaction of chlorine with sodium chlorite. Once the chlorine dioxide is generated as a gas, it is dissolved into the water to be treated. The gas flow rate is controlled to maintain a desired dose of chemical agent.

It has generally been found that chlorine dioxide provides superior inactivation with respect to a diverse number of microorganisms as compared to the more commonly used chlorine. For drinking water, it is effective against *cryptosporidium* and *giardia* which are of ongoing concern in the water supply.

An accurate, portable and reliable ClO_2 monitoring device could find a broad commercial use. The proposed hand held and inexpensive electrochemical ClO_2 monitor that is capable of monitoring ClO_2 levels in real-time with a detection limit of 2 ppb could be used for applications intended to control microbiological growth in a number of different industries, such as the dairy industry, the beverage industry, the pulp and paper industry, the fruit and vegetable industries, various canning plants, the poultry industry, the beef processing industry and miscellaneous food processing applications.

In addition to the applications mentioned above, the proposed ClO_2 monitor could also be used in chlorine dioxide generators to accurately control concentration of generated ClO_2 .